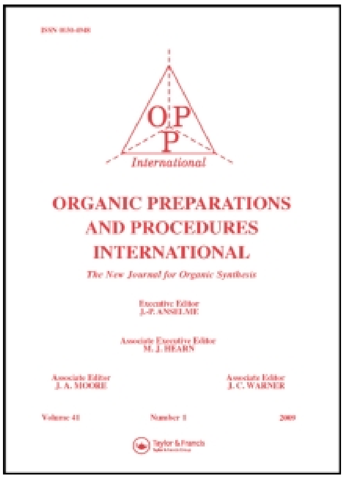

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SYNTHESIS OF NEW POLYMTROSTILBENES

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OPPI BRIEFS

SYNTHESIS OF NEW POLYNITROSTILBENES

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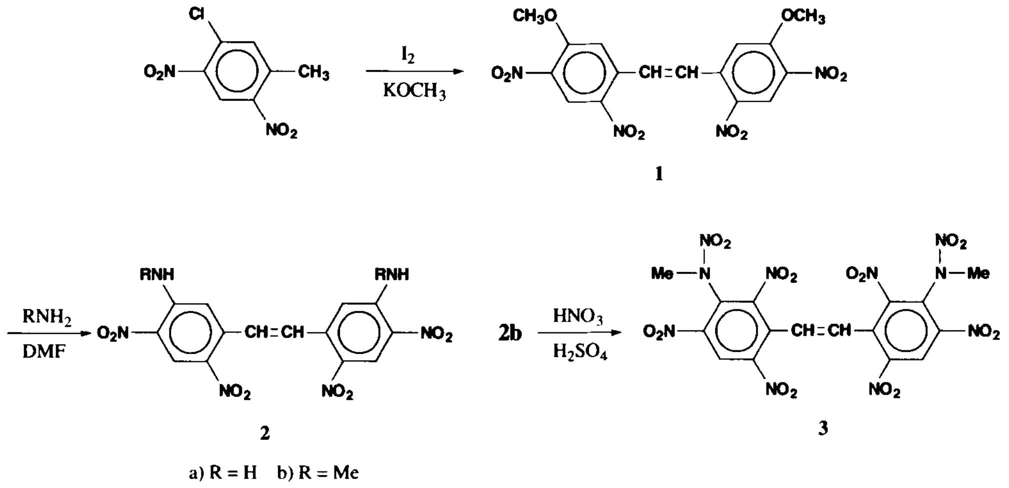
2,2',4,4',6,6'-Hexanitrostilbene (HNS) is a heat-resistant explosive which has been used more widely than any other.[1-4] Because of its thermal stability, special attention has been paid to polynitrostilbenes. In 1987, we developed a two-step synthesis of HNS which overcame the disadvantages of high-cost and low yield of the one-step method.[5] In 1978, Buckley and coworkers[6] suggested that compounds related to HNS might be prepared *via* oxidative coupling of 2,6-dimethyl-1,3,5,8-tetranitronaphthalene (mp. 302°) and of 2,6-dimethyl-1,3,5,7-tetranitronaphthalene (mp. 332°). On the basis of these results, we investigated synthetic approaches to polynitrostilbenes.

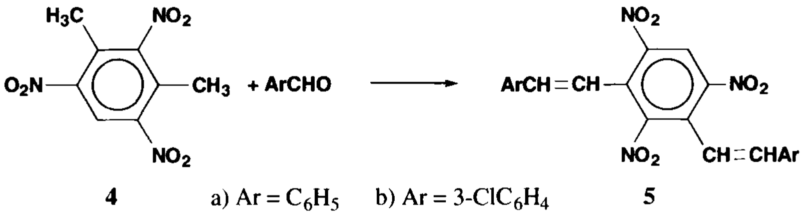
In organic solvents, polynitroarenes containing methyl groups might undergo oxidative coupling to give stilbenes in alkaline medium.[7-9] According to Shipp and Kaplan,[10] this method is suitable only for those nitroarenes in which the methyl possesses a certain degree of acidity (with sodium hypochlorite as oxidant). For example, sodium hypochlorite could be used to make HNS from 2,4,6-trinitrotoluene (TNT, pK_a 14.45) while 2,4-dinitrotoluene and 2,6-dinitrotoluene (pK_as 17.12 and 19.0 respectively) did not react under the same conditions. When sodium hypochlorite was used as the oxidant, Shipp and Kaplan suggested that the reaction proceeded *via* a carbanion intermediate, and then the presence of an electron-withdrawing group on the ring or the existence of p~π conjugation effect might facilitate the reaction. Therefore under conditions similar to Shipp's reaction, we attempted oxidative coupling of 2,4,6-trinitro-*m*-chlorotoluene (TNClT), 2,4,6-trinitro-*m*-xylene (TNX), 2,4,6-trinitro-*m*-aminotoluene (TNAT), 2,4-dinitro-*m*-chlorotoluene (DNClT) and 2,4-dinitro-*m*-acetyltoluidine (DNA_cT) with sodium hypochlorite, in the hope of obtaining HNS homologues directly; however, all these attempts failed. Shipp had also used iodine as oxidant and obtained HNS from TNT in 10% yield.[11] Thus we oxidized 2,4-dinitro-*m*-chlorotoluene by this method to 5,5'-dimethoxy-2,2',4,4'-tetranitrostilbene (**1**) in alkaline medium (Scheme 1). In order to obtain a compound of higher melting or decomposition point, energy density and effective oxygen content, it was decided to attempt the amination (or methylamination) and the nitration of **1**. Since side-reactions occurred (presence of strong C = O band at 1700 cm^{-1}) during nitration, **1** was then aminated and methylaminated. Displacement of CH_3O by the more nucleophilic NH_2 (CH_3NH) with excess aqueous ammonia or methylamine was carried out in DMF, 5,5'-diamino-2,2',4,4'-tetranitrostilbene (**2a**) and

5,5'-dimethylamino-2,2',4,4'-tetranitrostilbene (**2b**) were obtained respectively. While nitration of **2a** resulted in oxidation to give a product which showed a strong carbonyl absorption, **2b** gave 3,3'-dimethylamino-N,N',2,2',4,4',6,6'-octanitrostilbene (**3**).

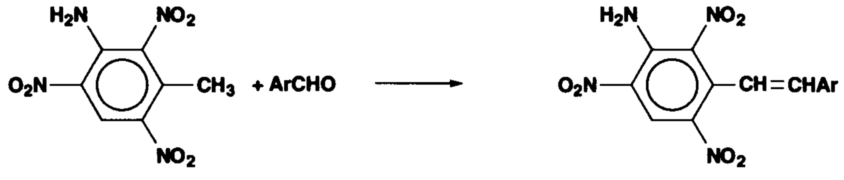


Scheme 1

Under basic conditions, toluenes activated by electron-withdrawing group might condense with aromatic aldehydes or ketones to form stilbenes.[12-15] Polynitrotoluenes such as TNAT, TNMP (trinitro-*m*-methylphenol), TNX, TNCIT and *as*-TNT (asymmetric 2,3,4-trinitrotoluene) obtained from the nitration of 3,4-dinitrotoluene were selected for reaction with benzaldehyde, *m*-hydroxy-, *m*-chloro- and *m*-nitrobenzaldehyde. In some cases, the amount of catalyst and the type of solvent were varied (*e. g.* using toluene, *m*-xylene or propanol instead of benzene) in order to increase reaction rate and shorten reaction time. While TNX did not react with *m*-hydroxybenzaldehyde and *m*-nitrobenzaldehyde, it condensed with two equivalents of benzaldehyde and of *m*-chlorobenzaldehyde to give 1,3-distyryl-2,4,6-trinitrobenzene (**5a**) and 1,3-di[3'-chlorostyryl]-2,4,6-trinitrobenzene (**5b**) (Scheme 2). TNAT reacted with the above-mentioned aldehydes as expected to produce the corresponding *trans* polynitrostilbenes **6a-d** (Scheme 3). It is interesting that in these cases, the aldehydes condensed with the methyl group rather than with the amino group. TNMP, TNCIT and *as*-TNT failed to react with these aldehydes under the same conditions.



Scheme 2



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a) Ar = C_6H_5 b) Ar = 3-HOC_6H_4 c) Ar = 3-ClC_6H_4 d) Ar = 3-$NO_2C_6H_4$

Scheme 3

Some of the new compounds synthesized may be useful as high energy explosive and may react further to produce polynitrostilbenes which could be of use as probes of the relationship between structure and heat-resistant properties of polynitrostilbenes.

EXPERIMENTAL SECTION

All chemicals and solvents are reagent grade or better. All melting points are uncorrected. Elemental analyses were obtained using a Perkin-Elmer 240C analyzer. IR spectra were determined as KBr pellets on a SP-7400 spectrometer or a Hitachi IR meter 260-10. ^1H NMR spectra were measured on a EX-90Q (90MHz) spectrometer in $(CD_3)_2CO$ solutions using TMS as internal standard. Mass spectra were recorded on a TSQ-45B.

5,5'-Dimethoxy-2,2',4,4'-tetranitrostilbene (1).- DNCIT (10.83 g, 0.05 mole) and pyridine (60 mL) were added into a 500 mL three-necked flat-bottomed flask equipped with a thermometer and a magnetic stirrer. The mixture was stirred at room temperature until a homogeneous brown solution was formed. Then a methanolic solution (148 mL) of iodine (18.7 g) was added dropwise over 20 min. The reaction mixture was cooled to -10° in an ice-salt bath and 33% methanolic potassium hydroxide solution (42 mL) was added dropwise over 50 min. The reaction mixture was stirred at -10° to -5° for 30 min, then warmed to room temperature and stirred for additional 20 min. The precipitated product was collected, washed with methanol (3 x 10 mL) and then with water (3 x 20 mL) and dried to yield 3.62 g (34%) of pale yellow solid. Recrystallization from acetone gave 2.98 g (28%) of pale yellow solid, mp. 232-233.5°. IR (cm^{-1}): 3060, 2960, 970. ^1H NMR: δ 8.66 (2H), 7.87-7.73 (4H, J = 16Hz, *trans*-CH=CH-), 4.20 (6H).

Anal. Calcd. for $C_{16}H_{12}N_4O_{10}$: C, 45.72; H, 2.88; N, 13.33. Found: C, 45.71; H, 2.61; N, 13.37

5,5'-Diamino-2,2',4,4'-tetranitrostilbene (2a).- To a solution of **1** (0.50 g) in DMF (20 mL) contained in a 100 mL three-necked flat-bottomed flask equipped with a magnetic stirrer was added 25%-28% aqueous solution (7 mL) of ammonia. The heavy yellow precipitate was stirred for 80 min at room temperature. The precipitated product was collected, washed with water and dried to yield 0.43 g (93%) of yellow solid. Recrystallization from acetone gave 0.39 g (84%) of yellow solid, mp. 345-346°. IR (cm^{-1}): 3450, 3350, 960.

Anal. Calcd. for $C_{14}H_{10}N_6O_8$: C, 43.08; H, 2.59; N, 21.54. Found: C, 43.37; H, 2.71; N, 21.73

5,5'-Dimethylamino-2,2',4,4'-tetranitrostilbene (2b) was prepared in a similar way to that of **2a** to yield 76% of **2b**, mp. 342-344°. IR (cm^{-1}): 3350, 1590, 970.

Anal. Calcd. for $C_{16}H_{14}N_6O_6$: C, 45.93; 3.38; N, 20.09. Found: C, 45.98; H, 3.15; N, 20.16

3,3'-Dimethylamino-N,N',2,2',4,4',6,6'-octanitrostilbene (3).- Compound **2b** (0.30 g) was placed in a 100 mL three-necked flat-bottomed flask equipped with a thermometer and a magnetic stirrer. Then 96% sulfuric acid (10 mL, $\delta = 1.84$) was added slowly with stirring, followed by the dropwise addition of fuming nitric acid (4 mL, $\delta = 1. 50$) at 20-25°. The mixture was stirred for 60 min and then diluted with flaked ice and water (200 mL). The precipitated product was collected, washed with water and dried to yield 0.22 g (51%) of pale yellow solid. Recrystallization from acetone-ethanol gave 0.19 g (44%) of pale yellow solid, mp. 228.2-228.9°. IR (cm^{-1}): 3100, 2800, 965. ^1H NMR: δ 9.22 (2H), 7.30-7.20 (2H, J = 16Hz, *trans*-CH=CH-), 3.70 (6H).

Anal. Calcd. for $C_{16}H_{10}N_{10}O_{16}$: C, 32.11; H, 1.69; N, 23.41. Found: C, 32.40; H, 1.58; N, 23.11

1,3-Distyryl-2,4,6-trinitrobenzene (5a).- TNX (24.10 g, 0.10 mole), benzene (200 mL), benzaldehyde (22.30 g, 0.21 mole) and piperidine (2 mL) were placed in a 500 mL flask fitted with a Dean-Stark trap. The mixture was refluxed for 15 hrs until water (3.5 mL) was collected in the trap. After evaporated of benzene (75-100 mL) ethanol was added dropwise to the residue until a precipitate appeared. Then, the mixture was cooled to room temperature and placed in a refrigerator overnight. The precipitated product was collected, washed and dried to yield 35.30 g (85%) of yellow orange solid. Recrystallization from acetone gave 33.60 g (80%) of yellow orange solid, mp. 149.5-151.1°. IR (cm^{-1}): 3060, 1570, 960. ^1H NMR: δ 8.94 (1H), 7.64-7.28 (10H), 7.02-6.84 (4H, J = 18Hz, *trans* -CH=CH-).

Anal. Calcd. for $C_{22}H_{15}N_3O_6$: C, 63.30; H, 3.63; N, 10.07. Found: C, 63.31; H, 3.57; N, 9.85

1,3-Di[3'-chlorostyryl]-2,4,6-trinitrobenzene (5b) was prepared in a similar way to that of **5a** to yield 85% of **5b**, mp. 142.5-143.1°. IR (cm^{-1}): 3060, 1585, 970. ^1H NMR: δ 9.02 (1H), 7.64-7.40 (8H), 7.02-6.84 (4H, J = 18Hz, *trans* -CH=CH-).

Anal. Calcd. for $C_{22}H_{13}Cl_2N_3O_6$: C, 54.32; H, 2.67; N; 8.64; Cl, 14.61
Found: C, 54.43, H, 2.64; N, 8.55; Cl, 14.60

3-Amino-2,4,6-trinitrostilbene (6a) was prepared in a similar way to that of **5a** to yield 58% of **6a**, mp. 184-186°. IR (cm^{-1}): 3470, 3370, 980.

Anal. Calcd. for $C_{14}H_{10}N_4O_6$: C, 50. 91; H, 3.06; N, 16.97. Found: C, 50.98; H, 3.01; N, 16.76

3-Amino-3'-hydroxy-2,4,6-trinitrostilbene (6b) was prepared in a similar way to that of **5a** to yield 48% of **6b**, mp. 220.8-221.5°. IR (cm^{-1}): 3470, 3370, 985. ^1H NMR: δ 9.10 (1H), 7.46-6.90 (7H), 6.80-6.60 (2H, J = 18Hz, *trans*-CH=CH-). MS (EI, *m*/e): 347 (M+1), 346 (M^+), 330, 301, 226, 195, 177, 151, 122, 107, 104, 78, 58, 43.

Anal. Calcd. for $C_{14}H_{10}N_4O_7$: C, 48.56; H, 2.92; N, 16.18. Found: C, 48.43; H, 2.97; N, 16.11

3-Amino-3'-chloro-2,4,6-trinitrostilbene (6c) was prepared in a similar way to that of **5a** to yield 50% of **6c**, mp. 216-217°. IR (cm^{-1}): 3470, 3360, 970. ^1H NMR: δ 9.14 (1H), 7.63 (2H), 7.56-7.36 (4H), 6.84-6.66 (2H, J = 18Hz, *trans*-CH=CH-). MS (EI, *m*/e): 366, 365 (M+1), 364 (M^+), 347, 301, 253, 224, 194, 176, 164, 150, 139, 125, 104, 90, 82, 77.

Anal. Calcd. for $C_{14}H_9ClN_4O_6$: C, 46.10; H, 2.49; N, 15.37; Cl, 9.72
Found: C, 46.32; H, 2.41; N, 15.38; Cl, 9.72

3-Amino-3'-nitro-2,4,6-trinitrostilbene (6d) was prepared in a similar way to that of **5a** to yield 74% of **6d**, mp. 225-227°. IR (cm^{-1}): 3460, 3350, 965.

Anal. Calcd. for $C_{14}H_9N_5O_8$: C, 44.80; H, 2.42; N, 18.67. Found: C, 44.87; H, 2.31; N, 18.76

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